Magnetic state and magnetic hysteresis in the molybdenum diselenide intercalated with chromium atoms

Journal of Physics: Conference Series **1389** (2019) 012029 doi:10.1088/1742-6596/1389/1/012029

Magnetic state and magnetic hysteresis in the molybdenum diselenide intercalated with chromium atoms

V G Pleshchev, D S Neznakhin, V S Flyagin, N V Selezneva

Institute of Natural Sciences and Mathematics, Ural Federal University named after B.N. Yeltsin Ekaterinburg, Russian Federation.

Abstract. In this work intercalated compounds in the Cr-$MoSe_2$ system were synthesized for the first time. Their magnetic properties are studied at various intercalant concentrations, temperatures and magnetic fields. The temperature dependences of effective magnetic moments and positive paramagnetic Curie temperatures in the paramagnetic region evidence the feasible ferromagnetic interactions between intercalated atoms. The existence of low-temperature ferromagnetic state in Cr_xMoSe_2 is confirmed by hysteresis phenomena in temperature dependences magnetic susceptibility and field dependences of magnetization. The change in the magnetic state affects the character of the temperature dependences of the resistivity.

The creation and research of materials with reduced dimensionality has attracted increasing attention in recent decades, since such materials may have interesting physical properties and unique characteristics from the point of view of their possible practical application. Transition metal (T) dichalcogenides TX_2 (X = chalcogen) having a quasi-two-dimensional character of the crystal structure can be attributed to such systems. The intercalation of 3d-metal (M) atoms having a magnetic moment into TX_2 leads to the formation of compounds with different magnetic behaviors from paramagnetic and spin-glass type to magnetically ordered states. The properties of intercalated transition metal dichalcogenides M_xTX_2 are found to depend both on the type of inserted M atoms and on the type of the starting compound. For example, the magnetic order of the antiferromagnetic type was found in the compounds Cr_xTiSe_2 and Fe_xTiSe_2, while the behavior of magnetization in the compounds Cr_xTiTe_2 and Fe_xHfS_2 was associated with the presence of a ferromagnetic order [1-3]. The presence of magnetic ordering in M_xTX_2 compounds with a layered crystal structure results from the competition of intralayer and interlayer exchange interactions of different types between the 3d electrons of the inserted M atoms [4]. The combination of super-exchange and RKKY-type exchange interactions is suggested to be responsible for the magnetic order in M_xTX_2. Within the family of intercalated molybdenum dichalcogenides MoX_2 (X = S, Se), the $FeMo_2S_4$ ($Fe_{0.5}MoS_2$) compound exhibits an antiferromagnetic order below 110 K, as evidenced by neutron diffraction studies [5].

Molybdenum dichalcogenides MoX_2 (X = S, Se), like the similar compounds of the elements of group 4 of the periodic table (e.g., titanium dichalcogenides), have a layered crystal structure. However, the structural difference is that TiX_2 is characterized by a 1T modification with octahedral coordination of titanium atoms, whereas molybdenum diselenide can have various structural modifications (polytypes) such as 2H-$MoSe_2$ and 3R-$MoSe_2$, differing in the position of atoms and the number of $MoSe_2$ layers in the unit cell. The 2H-$MoSe_2$ modification is described by the hexagonal structure (space group $P6_3/mmc$). The unit cell of 2H-$MoSe_2$ contains two $MoSe_2$ layers with a trigonal-prismatic environment of molybdenum atoms [6, 7].

The initial molybdenum diselenide and intercalated intercalated Cr_xMoSe_2 samples (x = 0.1-0.5) were synthesized from the initial elements by the method of solid-phase reactions in evacuated quartz ampoules in two stages. This technology was previously repeatedly used for the synthesis of intercalated materials based on titanium dichalcogenides and was described in detail earlier [1, 2]. X-ray certification showed a single-phase state of the obtained samples and their structure corresponded to the 2H-$MoSe_2$ modification. This is demonstrated by diffractograms for several samples, shown in figure 1. It also shows the result of comparing the experimental data with the structural model (bottom line). The magnetic properties of the samples were measured using a Quantum SQUID magnetometer (MPMS) in the temperature range of 2 – 350 K and in magnetic fields up to 70 kOe.

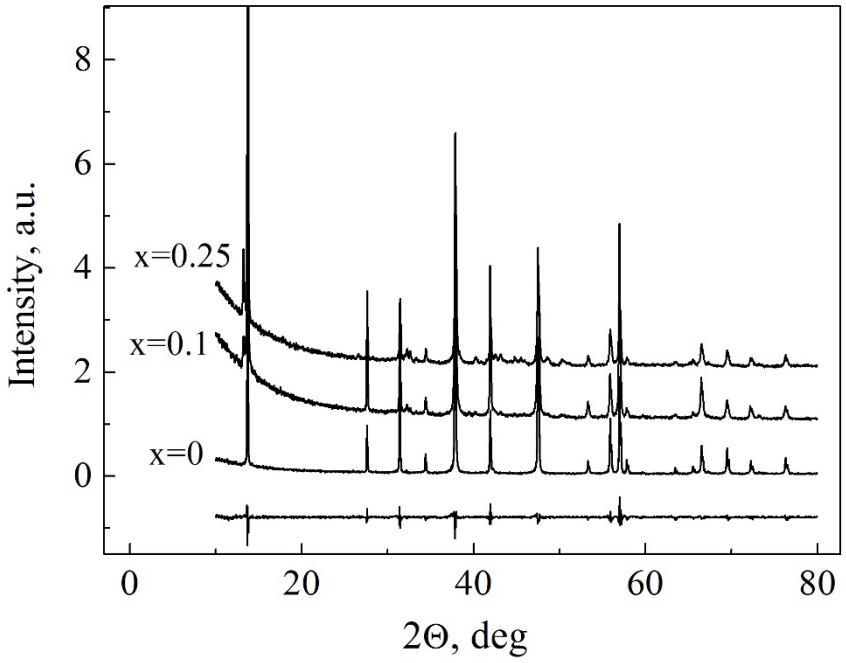

Figure 1. X-ray diffraction pattern of the Cr_xMoSe_2 samples. The bottom line represents the difference between experimental values of intensity and the calculated values.

The temperature dependences of the magnetic susceptibility (χ) when T > 150K were well described by the generalized Curie-Weiss law.

$$\chi(T) = \chi_0 + C/(T - \Theta p) \quad (1)$$

From analysis of the χ(T) dependences measured in the high temperature region, the effective magnetic moment, μeff, on chromium atoms intercalated into $MoSe_2$ was determined. The values of μ_{eff} calculated per Cr ion are found to vary in the Cr_xMoSe_2 system ($0.1 < x \leq 0.5$) within the range (3.52 – 4.05) μ_B, i.e. close to the spin value $\mu_{eff} = 3.87\ \mu_B$ for Cr^{3+} ion at g = 2. These data indicate that 3d electrons of Cr ions remain well localized after intercalation into $MoSe_2$. For all the Cr_xMoSe_2 compounds, the paramagnetic Curie temperatures, Θ_p, were obtained to be positive, which indicates the dominance of the ferromagnetic exchange interaction between chromium 3d electrons. The existence of this interaction was additionally confirmed by the dependences of the effective magnetic moments in the temperature range of 100–350 K, which were derived from the formula below:

$$\mu_{eff} = (8 \cdot \chi_{mol}\, T/x)^{1/2} \quad (2)$$

where χ_{mol} is the molar susceptibility of compounds, T is a temperature, and x is a chromium content in Cr_xMoSe_2. In this expression, the χ_{mol} was evaluated from the specific value χ by excluding the temperature-independent χ_0 component. This allowed one to take into account only the Curie–Weiss contribution (the second term in expression 1) in the calculation of μ_{eff}. The data simulated for specimens with various compositions are available in figure 2. As seen, the μ_{eff} values at temperatures above 150 K remain constant. One can hence conclude that this temperature range is referred to the paramagnetic phase of specimens. With decreasing temperature, the values μ_{eff} for each specimen increase, which is related to the exchange enhancement of paramagnetism because of the ferromagnetic interaction between magnetoactive ions.

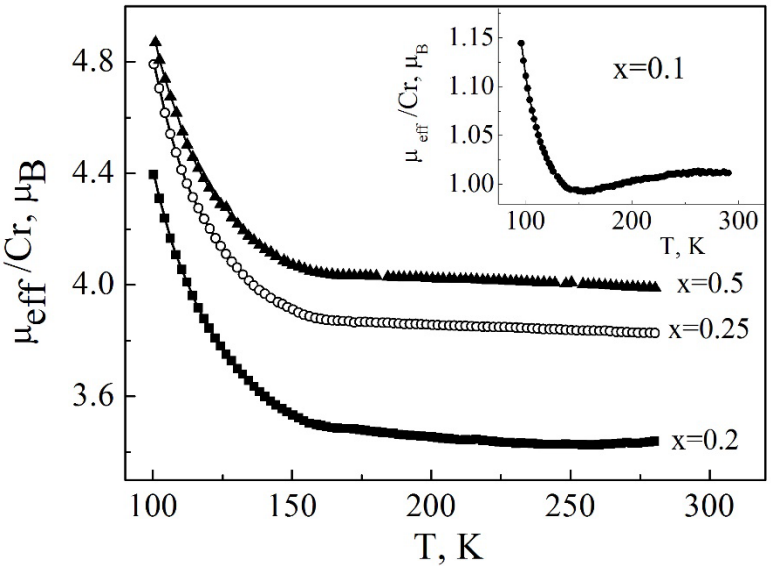

Figure 2. Temperature dependences of the effective magnetic moments of the Cr_xMoSe_2 samples.

The lower-temperature dependences $\chi(T)$ measured in the ZFC and FC modes for all samples are found to be irreversible (figure 3). The dependences obtained in the ZFC mode reveal a wide maximum at temperatures T_k, which is shifted towards higher temperatures with increasing chromium content. From these data, the value of the temperature of the magnetic phase transformation (Curie temperature), which is approximately 80–85 K, can be estimated.

The low temperature ferromagnetic state is confirmed by the presence of magnetic hysteresis loops when the magnetic field changes (figure 4). These loops are symmetric for all samples and characterized by a coercive force of about 3 kOe. The hysteresis loop area increases with chromium content mainly due to the rising magnetization. Bearing in mind positive values of Θ_p all these data are indicative of the appearance of a long-range magnetic order of the ferromagnetic type in the intercalated Cr_xMoSe_2 compounds.

Estimation of the average spontaneous magnetic moment per Cr atom from the magnetization data for $Cr_{0.25}MoSe_2$ and $Cr_{0.5}MoSe_2$ presented in figure 4 gives a value of about 0.51 μ_B and 0.64 μ_B respectively, which is substantially lower than the expected spin-only value 3 μ_B for Cr^{3+}. The magnetization of Cr_xMoSe_2 does not reach saturation even with an increase in the magnetic field up to 70 kOe, which together with reduced spontaneous magnetic moment may by indicative of the presence of a non-collinear magnetic structure with a ferromagnetic component and substantial magnetic anisotropy. Neutron diffraction measurements are needed to confirm this suggestion. It should be also noted that on-collinear magnetic structures were observed in some other transition metal dichalcogenides intercalated with Cr atoms.

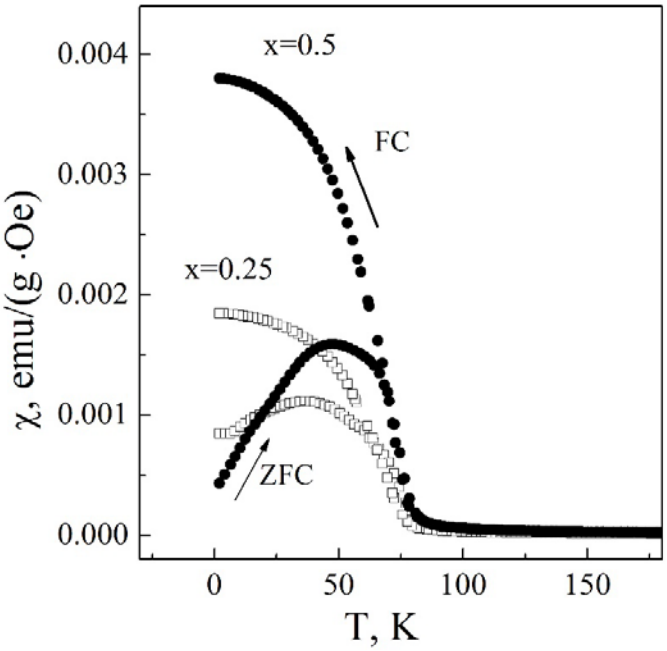

Figure 3. Temperature dependences of the magnetic susceptibility of Cr_xMoSe_2 compounds obtained in ZFC and FC regimes.

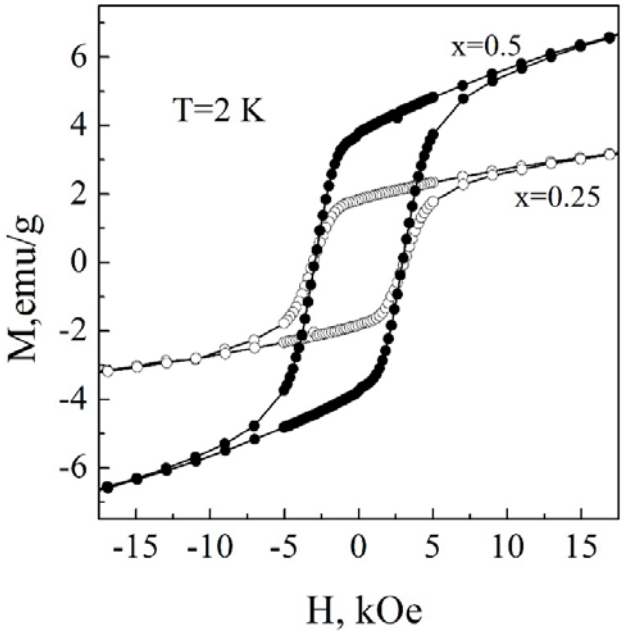

Figure4. Field dependences of magnetization of the Cr_xMoSe_2 compounds.

When measuring the electrical resistance of the obtained samples are made in the range of 6–350 K, it was noted that the change in the magnetic state of the Cr_xMoSe_2 samples with a change in temperature also affects the temperature dependences of the electrical resistance. These data are shown in figure 5. At low concentrations of chromium ($x \leq 0.25$), these dependences are non-monotonic and characterized by a maximum, and at $x = 0.33$ and $x = 0.5$ they indicate the metallic state of the samples in the entire

temperature range but experience a kink. In either case, the character of the temperature dependences changes at temperatures of 80–100 K, which corresponds to the transition from the paramagnetic state to the ferromagnetic state.

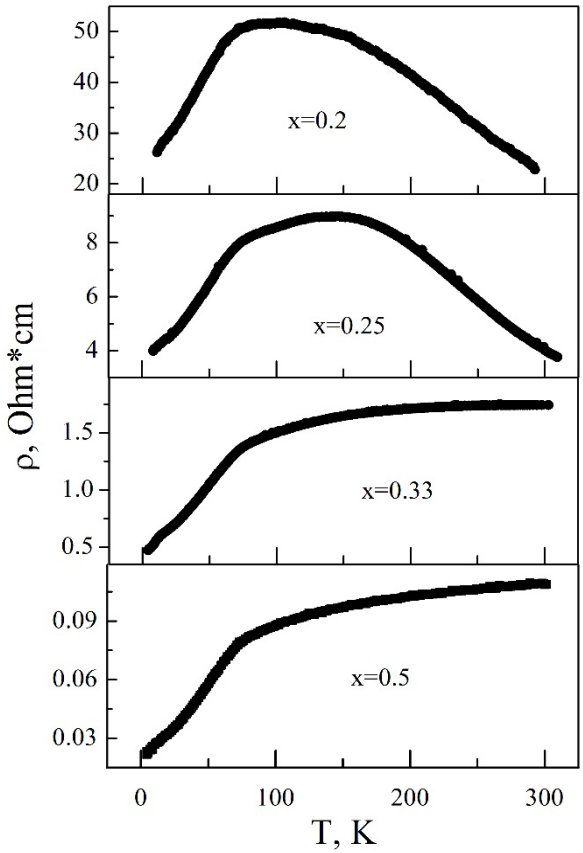

Figure 5. Temperature dependences of the electrical resistance of Cr_xMoSe_2 compounds.

In addition, it can be seen that with an increase in the chromium content, the electrical resistance of the samples decreases. This is probably due to an increase in the concentration of charge carriers introduced with chromium ions. In this case, the indirect exchange interaction is taken into account when determining the nature of the magnetic state.

Acknowledgments
This work was supported by the Ministry of Education and Science of the Russian Federation (project No 3.2916.2017/4.6).

References
[1] Baranov N V, Pleshchev V G, Selezneva N V, Sherokalova E M, Korolev A V, Kazantsev V A and Proshkin A V 2009 *J. Phys.: Condens. Matter*. **21** 506002
[2] Selezneva N V, Baranov N V, Pleshchev V G, Mushnikov N V and Maksimov V I 2011 *Solid State Phen.* **53** 308
[3] Pleshchev V G, Selezneva N V 2018 *Phys. Solid State*. **60** 250
[4] Tazuke Y, Shibata S, Nakamura K and Yano H 1995 *J. Phys. Soc. Jpn*. **64** 242
[5] Vaquero P, Kosidowski M L and Powell A V 2002 *Chem. Mater*. **14** 1201
[6] Kalikhman V L, Umanskii Ya S 1973 *Sov. Phys. Usp.***15** 728
[7] James P B, Lavik M T 1963 *Acta cryst.* **16** 1183